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Novel Five- and Six-Membered Rings of Phosphorus−Selenium Heterocycles from Selenation of Amido-Schiff Bases

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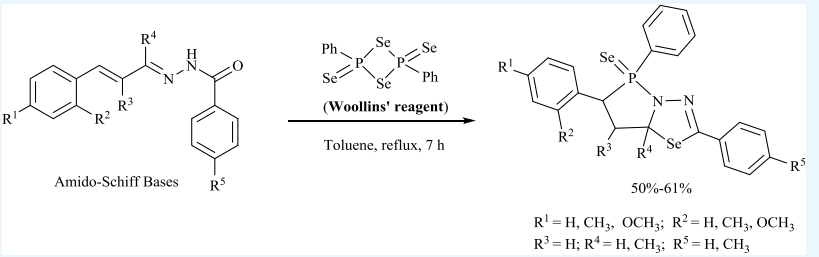

ABSTRACT: Woollins' reagent, [2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide], serving as a selenating-reductive cycloaddition reagent, reacts with nonconjugated amido-Schiff bases to give the corresponding six-membered 1,3,4-selenadiazoles via a ring-expansion accompanied by an additional selenation/cyclization to the imine bond and C═O group; meanwhile, under the same reaction conditions, the selenation of conjugated amido-Schiff bases leads to a series of fused heterocycles with two five-membered rings. Eight single-crystal X-ray structures confirming the formation of these five- and six-membered heterocycles are discussed.

INTRODUCTION

Schiff bases have diverse pharmacological activities as well utility as corrosion inhibitors, insecticides, and pesticides[1−3] and are among the most widely used reagents and intermediates in organic synthesis and ligands in coordination chemistry.[4−11] However, there are still many reactivities that need to be explored. Staudinger first studied [2 + 2] cycloadditions with ketenes to give b-lactams in 1907.[12] Corey et al. utilized this cycloaddition reaction successfully for the first laboratory synthesis of penicillin in 1950.[13] Since then, few studies on the cycloaddition to C═N bonds have been reported. Mathey et al. reported that a methoxy-substituted phosphinidene adds to 1-azadienes, giving 1,4-adducts, five-membered ring 1,2-azaphospholenes.[14] Streubel et al. used 1,2-addition to a C═N bond, resulting in the formation of the azaphosphiridine complex from the thermal decomposition of the 2*H*-azaphosphirene complex in the presence of imine.[15] Phosphinidene complexes, generated from the corresponding 7-phosphanorbornadienes, react with an excess of imine [Ph−CH═N−Me], leading to the five-membered 1,4,2-diazaphospholanes.[16] Phosphinidene complexes can also react with diimines [PhCH═N−$(CH_2)_n$−N═CHPh, n = 2, 3, 4], giving bicyclic $(CH_2)_n$ bridged diazaphospholanes.[17]

The chemistry of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide (Woollins' reagent, WR) has been developed and exploited widely by us and other groups as a versatile selenation reagent or synthetic precursor in synthetic chemistry.[18−31] Recently, we have reported that Woollins' reagent can add to the C═N bond of a series of conjugated Schiff bases to generate a series of stable five-membered phosphorus−selenium−nitrogen heterocycles.[32] In continuation of our interest in the chemistry of WR toward various organic substrates, we report herein the reactivity of WR toward amido-Schiff bases, which led to the formation of a series of five- and six-membered P−Se heterocycles and their related X-ray structures. To the best of our knowledge, this is the first reported synthesis and single-crystal structures of such small ring phosphorus−selenium heterocycles incorporating single Se−P═Se or N−P═Se linkage.

RESULTS AND DISCUSSION

The selenation of N-substituted benzylidenebenzohydrazides **1** and **2** by WR afforded new six-membered phosphorus−selenium heterocycles **3** and **4** in 56 and 46% yield, respectively (Scheme 1). It can be suggested that the formation of heterocycles **3** and **4** results from the addition of an equilibrium monomeric species $PhPSe_2$,[33] arising from WR into the C═N bond of the unsaturated Schiff bases **1** and **2** to generate an unstable intermediate **I**, the latter is able to carry

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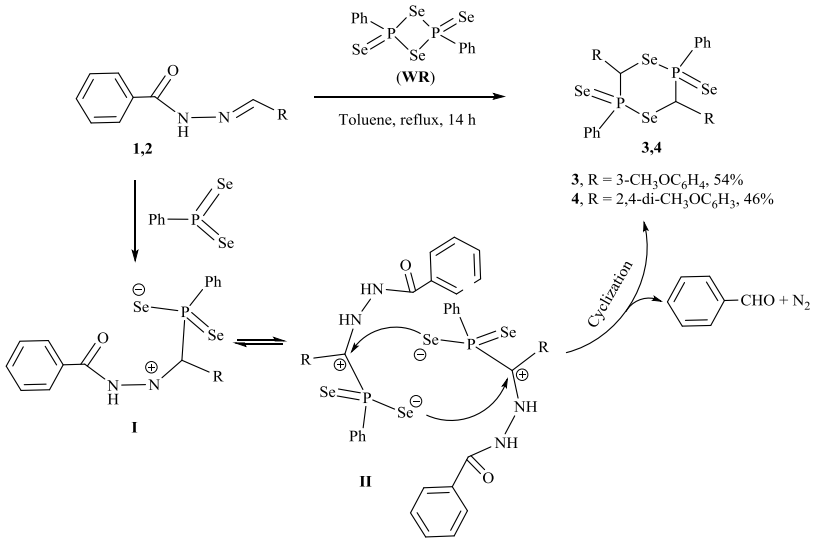
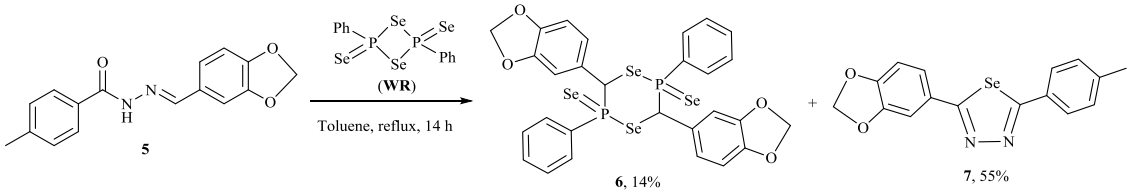
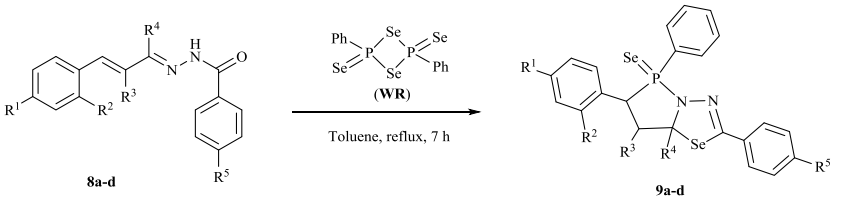
Scheme 1. Synthesis of the Six-Membered Phosphorus−Selenium Heterocycles 3 and 4



Scheme 2. Formation of the Heterocyclic Compounds 6 and 7



Scheme 3. Preparation of the Fused Five-Membered Rings 9a−d



9a, $R^1 = R^2 = R^3 = H$, $R^4 = CH_3$, $R^5 = CH_3$, 52%
9b, $R^1 = H$, $R^2 = OCH_3$, $R^3 = R^4 = H$, $R^5 = CH_3$, 50%
9c, $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = CH_3$, 61%
9d, $R^1 = R^2 = R^3 = H$, $R^4 = CH_3$, $R^5 = H$, 60%

out an intermolecular coupling reaction **II** to give the final products heterocycles **3** and **4** by further loss of two molecules of benzaldehyde and two molecules of N_2. The ^{31}P NMR spectra of heterocycles **3** and **4** show broad singlets at 45.6 and 46.4 ppm, respectively, flanked by selenium satellites with $^{31}P-^{77}Se$ coupling constants of 380/373 and 752/759 Hz; and the ^{77}Se NMR spectra display double doublets at 461.4/338.7 and −215.2/−213.0 ppm with the matching coupling constants, indicating the presence of single P−Se bonds and double P═Se bonds in both compounds.

Interestingly, under identical reaction condition, benzohydrazide **5** reacts with WR to the give five-membered 2-(benzo[*d*][1,3]dioxol-5-yl)-5-(*p*-tolyl)-1,3,4-selenadiazole **7** in 55% yield together with the expected six-membered phosphorus−selenium heterocycle **6** in 14% yield (Scheme 2). The same reaction mechanism (Scheme 1) can be used to rationalize the formation of **6**, and we have previously reported that reaction of 1,2-diacylhydrazines or carbohydrides with WR results in symmetrical 2,5-disubstituted 1,3,4-selenadiazoles,[20,29] and therefore the formation of **6** is not surprising, following a similar route. Two diastereomers in ca. 1:1 intensity ratio were identified in the ^{31}P NMR spectrum of compound **6**, which shows two wide singlet signals along with matching selenium satellites as found in compounds **3** and **4**. The ^{77}Se NMR for selenium-containing heterocycle **7** displays a singlet peak at 769.0 ppm, which is consistent with its analogues.[20,29]

However, in contrast to the above results, the reaction of WR with conjugated amido-Schiff bases **8a−d** under the similar conditions led to a series of unexpected fused phosphorus−selenium−nitrogen heterocycles **9a−d** in good yields (50−61%), as shown in Scheme 3. The reaction mechanism is not clear; we can surmise that the formation of these fused heterocycles might be via selenation/cyclization/cycloaddition, but whether this happened simultaneously or successively is unknown. The ^{31}P NMR spectra of these fused heterocycles **9a−d** show only singlets at 65.2−78.8 ppm, with the corresponding selenium satellites ranging from 816 to 822 Hz. One doublet and one singlet were observed in the ^{77}Se NMR spectrum for each compound.

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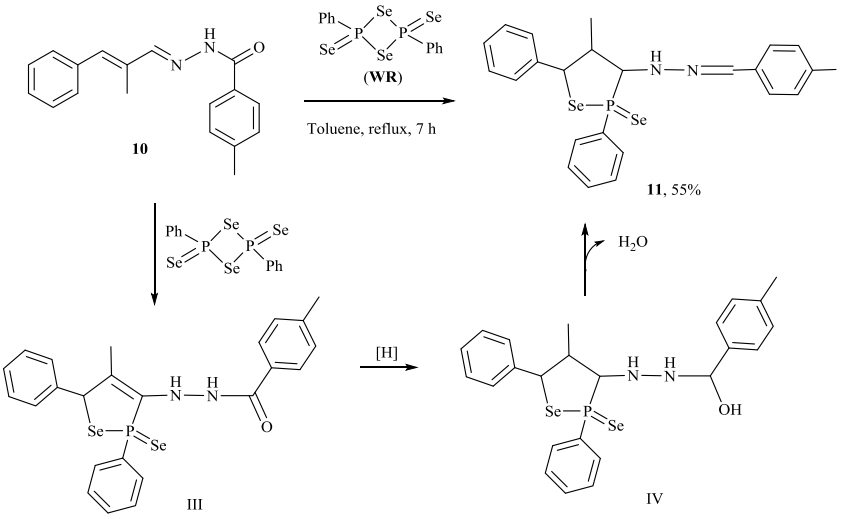
Scheme 4. Preparation of the Five-Membered Ring 11



Another interesting result is from the reaction of WR with 4-methyl-*N*′-(2-methyl-3-phenylallylidene)benzohydrazide **10**, which led to a five-membered phosphorus−selenium heterocycle **11** in 55% yield (Scheme 4) rather than the fused compounds as shown in Scheme 3. The formation of this compound might first proceed by a [3 + 2] cycloaddition of the Schiff base with a reactive species $PhPSe_2$[33] from WR to give an intermediate **III**, which is then reduced to deliver an intermediate **IV**, in which the C═C and C═O groups are further reduced to the corresponding saturated sp^3 C−C and CH(OH) groups. The final product **11** would then be obtained via a dehydration reaction with the loss of a molecule of water from the intermediate **IV**. The ^{31}P NMR spectrum of **11** reveals one singlet at 59.9 ppm, accompanied by two sets of selenium satellite peaks with a coupling constants of 382/748 Hz. Two selenium signals at 387.1 and −207.8 ppm with matching coupling constants were observed in its ^{77}Se NMR spectrum.

Crystals of heterocyclic compounds **3**, **4**, **6**, **7**, **9a**, **9c**, **9d**, and **11** suitable for X-ray crystallographic analysis were grown by the diffusion of hexane into a dichloromethane solution of the compound in air at room temperature (Tables S1 and S2).

The X-ray crystal structures of **3**, **4**, and **6** confirm the presence of the six-membered rings in pseudo-chair conformations, as shown in Figures 1−3. The P═Se groups are axial and the organic substituents are equatorial in all three structures. The dihedral angle between two substituted benzene rings/two phenyl rings and the P−C−Se−P−C−Se mean plane are 83.35 and 80.78° for **3**, 86.53 and 63.49° for **4**, and 77.55 and 76.04° for **6**. Within **3**, **4**, and **6**, the P−Se single-bond lengths are in the range of 2.2484(15)−2.253(2) Å and P═Se double-bond lengths in the range of 2.0879(18)−2.0965(7) Å; similar with those found in acyclic structures containing the P−Se−Se−P linkage.[34] The cross-ring P···P distances are marginally shorter than the sum of the van der Waals radii of two phosphorus atoms (3.9 Å), being 3.780, 3.770, and 3.712 Å in **3**, **4**, and **6**, respectively; as expected, these distances are significantly longer than those observed in

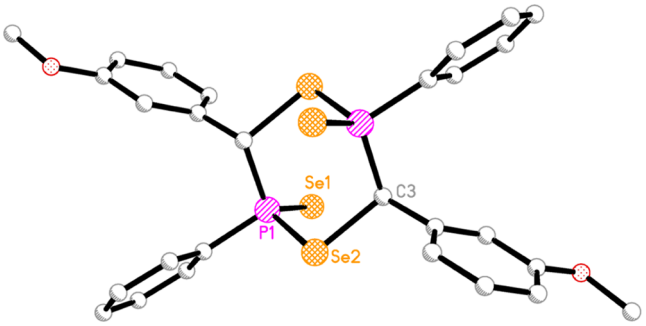


Figure 1. X-ray structure of compound **3**, with hydrogen atoms omitted for clarity.

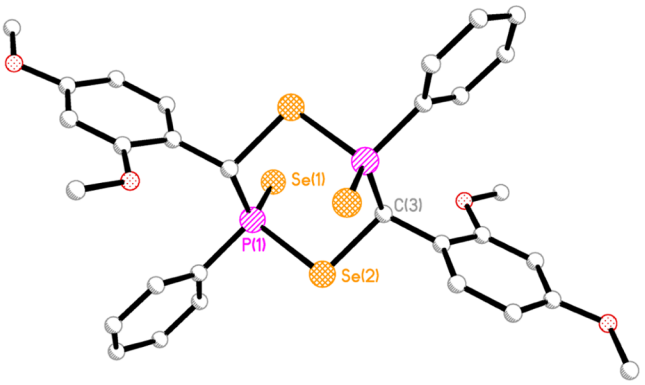


Figure 2. X-ray structure of compound **4**, with hydrogen atoms omitted for clarity.

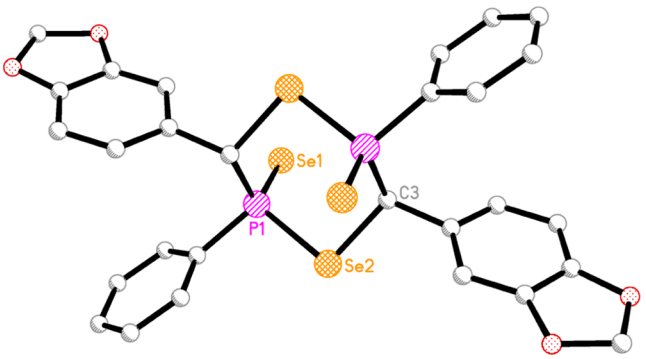


Figure 3. X-ray structure of compound **6**, with hydrogen atoms omitted for clarity.

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the four-membered P_2Se_2 ring system [3.1(1) Å], but, significantly shorter than those observed in the six-membered P_2Se_4 ring system [4.3(1) Å].[35] The geometry around the phosphorus atom is distorted tetrahedral with Se−P−Se: 114.67(9)° for **3**, 115.40(3)° for **4**, and 115.03(7)° for **6**, being considerably smaller than that observed in the six-membered P_2Se_4 ring system [117.78(6)−120.4(2)°].[35]

The overall molecular structure of **7** (Figure 4) is very similar to the previously reported analogous structures.[35] The

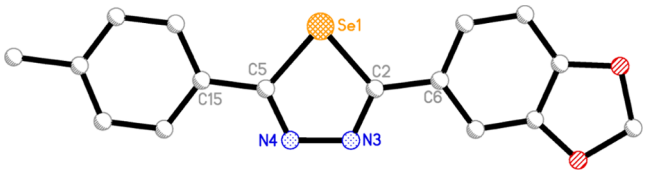

Figure 4. X-ray structure of compound **7**, with hydrogen atoms omitted for clarity.

C_2N_2Se ring is almost co-planar with the two aromatic substituents [the torsion angles to the substituents are 179.0(4) and 174.0(3)°]. The C−Se bond distances [1.876(5) and 1.873(5) Å] and the C−Se−C angle [82.6(2)°] are in good agreement with other 2,5-disubstituted 1,3,4-selenadazoles reported in the literature [C−Se bond lengths: 1.87−1.89 Å and C−Se−C angles: 81.9−82.7°].[20]

Three fused compounds **9a**, **9c**, and **9d** have similar frameworks (Figures 5−7). The dihedral angles between the

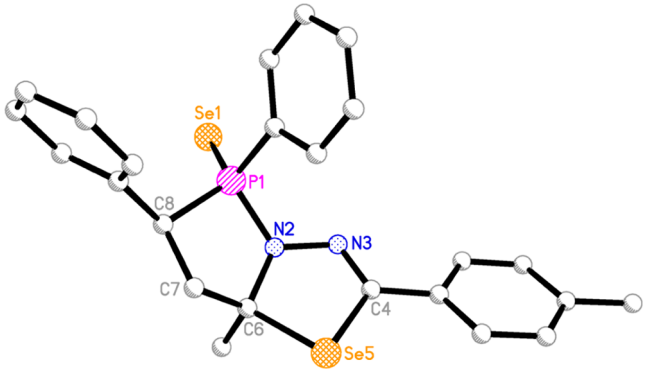

Figure 5. X-ray structure of compound **9a**, with hydrogen atoms omitted for clarity.

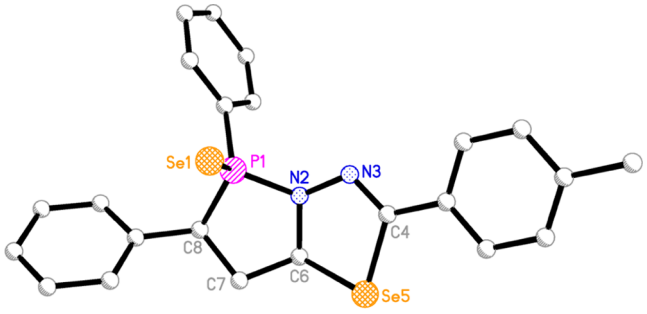

Figure 6. X-ray structure of compound **9c**, with hydrogen atoms omitted for clarity.

PNC_3 and the SeC_2N_2 mean planes are 31.88° for **9a**, 32.05° for **9c**, and 39.07° for **9a**, suggesting steric effects from the different aromatic rings. Similar effects are also observed on the

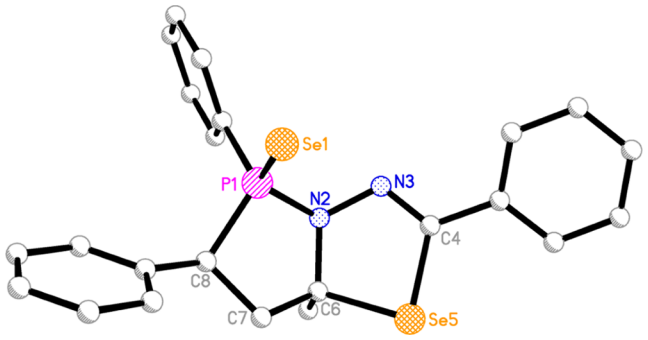

Figure 7. X-ray structure of compound **9d**, with hydrogen atoms omitted for clarity.

dihedral angles between the aromatic rings and the heterocycles [the angles between two phenyl rings and the mean plane of five-membered PNC_3 ring are 84.89 and 76.21° for **9a**, 70.49 and 58.66° for **9c**, and 78.46 and 68.20° for **9d**; the angles between the attached aromatic ring and the mean plane of five-membered N_2C_2Se ring are 19.23° for **9a**, 2.26° for **9c**, and 21.43° for **9d**]. The C(6)−N(2) bond lengths [1.479(2) Å for **9a**, 1.482(6) Å for **9c**, and 1.489(3) Å for **9d**] are similar to each other, marginally longer than the usual single-bond length of 1.47 Å.[36] The N(3)−C(4) bond distances [1.282(2) Å for **9a**, 1.274(6) Å for **9c**, and 1.278(3) Å for **9d**] are significantly shorter than that found in the five-membered P_2SeCN ring system [1.283(3)−1.339(3) Å],[19] suggesting that they are rare samples of an antiperiplanar [1,3,4]selenadiazole 5-selenide. The P═Se bond lengths [Se(1)−P(1): 2.0916(5) Å for **9a**, 2.0880(15) Å for **9c**, and 2.0897(6) Å for **9d**] in **9a**, **9c**, and **9d** are normal and comparable with those found in the five-membered heterocyclic compounds in the literature.[19,37−41] The geometries around P(1) [Se(1)−P(1)−N(2): 117.75(6)° for **9a**, 118.58(16)° for **9c**, and 118.01(7)° for **9d**] are somewhat distorted tetrahedral due to the effects of the steric hindrance of the attached phenyl groups.

The molecular structure of **11** adopts (Figure 8) a central five-membered twist $PSeC_3$ ring conformation. One tolyl ring

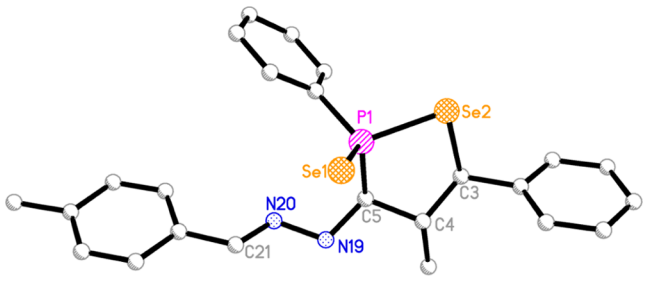

Figure 8. X-ray structure of compound **11**, with hydrogen atoms omitted for clarity.

substituent attached to an sp^2-carbon is twisted with respect to the $PSeC_3$ ring (the angle between the tolyl ring and the mean plane of $PSeC_3$ ring is 70.67°), while the other two phenyl rings attached to an sp^3-carbon and a P(V) atom point to the opposite sides of the cavity with dihedral angles of 76.14 and 78.85°. The P−Se single-bond length [2.2412(6) Å] is marginally shorter than that found in the similar five-membered $PSeC_3$ unit [2.2523(9) Å]; however, the double P═Se bond distance [2.1030(6) Å] is significantly longer than

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that observed in the similar five-membered $PSeC_3$ unit [1.941(3) Å],[42] indicating some degree of delocalization of π-electrons over the Se−P−Se fragment.

In summary, a highly efficient preparative route was developed to synthesize a series of novel five-membered and six-membered organophosphorus−selenium−nitrogen heterocycles via the direct reaction of the four-membered ring selenation reagent-2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide (Woollins' reagent) and amido-Schiff bases in refluxing toluene. Eight representative X-ray structures confirm the formation of these heterocycles. The reported results enhance the library of small membered phosphorus−selenium heterocycles.

EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were carried out under oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques; subsequent chromatographic and workup procedures were performed in air. Woollins' reagent was synthesized by following the reported method.[43] All amido-Schiff bases (N-substituted benzylidenebenzohydrazides **1**, **2**, **5**, **8a−d**, and **10**) were prepared by the reaction of benzoic hydrazide with substituted benzaldehydes in the presence of a few drops of acetic acid as a catalyst according to the literature method.[44] ^{1}H (400.1 MHz), ^{13}C (100.6 MHz), and ^{31}P-{^{1}H} (162.0 MHz) were recorded at 25 °C on a Noah Bruker Advance II 400s, and ^{77}Se-{^{1}H} (51.4 MHz referenced to external Me_2Se) NMR spectra was recorded at 25 °C on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000−250 cm^{-1} on a Perkin-Elmer 2000 FTIR/Raman spectrometer. The University of St Andrews microanalysis service performed microanalysis. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea, and the University of St Andrews Mass Spectrometry Service.

X-ray diffraction data were collected either at 93 K using a Rigaku MM007 High Brilliance RA generator/confocal optics and Mercury CCD system, or at 173 K using a Rigaku FR-X Ultrahigh Brilliance Microfocus RA generator/confocal optics and XtaLAB P200 diffractometer system. Both systems used Mo Kα radiation (λ = 0.71075 Å). Intensity data were collected using either ω and φ or just ω steps, accumulating area detector images spanning at least a hemisphere of reciprocal space. Data for all compounds analyzed were collected and processed (including correction for Lorentz, polarization, and absorption) using CrystalClear.[45] Structures were solved by either Patterson (PATTY)[46] or charge-flipping (SUPERFLIP)[47] methods and refined by full-matrix least-squares against F^2 (SHELXL).[48] Nonhydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model, except for the NH hydrogen in **11**, which was located from the difference Fourier map and refined isotropically subject to a distance restraint. All calculations were performed using the CrystalStructure interface.[49] CCDC 1979690−1979697 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Synthesis of 3,6-Bis(3-methoxyphenyl)-2,5-diphenyl-1,4,2,5-diselenadiphosphinane 2,5-diselenide (3). A suspension of *N*′-(3-methoxybenzylidene)benzohydrazide **1** (0.255 g, 1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in 20 mL of dry toluene was refluxed for 7 h. Upon cooling to room temperature and removing toluene in vacuum, the residue was purified by silica gel column (eluent 1:1 ethyl acetate/toluene) to give **3** as a gray solid (0.140 g, 54%). Melting point: 110−112 °C. Selected IR (KBr, cm^{-1}): 1596(m), 1580(m), 1488(m), 1434(s), 1261(s), 1143(m), 1041(m), 927(m), 906(m), 757(m), 687(vs), 528(m), 480(m). ^{1}H NMR (CD_2Cl_2, δ), 8.00−7.06 (m, 18H), 3.92 (s, 6H), 3.82 (m, 2H) ppm. ^{13}C NMR (CD_2Cl_2, δ), 159.7, 159.4, 146.9, 146.7, 132.9, 132.4, 132.2, 130.2, 129.0, 128.7, 128.6, 128.4, 127.3, 125.8, 114.8, 114.6, 113.4, 113.2, 55.3, 37.4, 37.1 ppm. ^{31}P NMR (CD_2Cl_2, δ), 45.6 (s, J(P,Se) = 380/782 Hz). ^{77}Se NMR (CD_2Cl_2, δ), 461.4 (d, J(P,Se) = 380 Hz), −215.2 (d, J(P,Se) = 782 Hz) ppm. MS (CI$^+$, m/z), 775 [M + H]$^+$. Accurate mass measurement [CI$^+$, m/z]: 775.8230 [M + H]$^+$, calculated mass for $C_{28}H_{26}N_2P_2Se_4H$: 775.8233.

Synthesis of 3,6-Bis(2,4-dimethoxyphenyl)-2,5-diphenyl-1,4,2,5-diselenadiphosphinane 2,5-diselenide (4). A suspension of *N*′-(2,4-dimethoxybenzylidene)-benzohydrazide **2** (0.284 g, 1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in 20 mL of dry toluene was refluxed for 7 h. Upon cooling to room temperature and removing toluene in vacuum, the residue was purified by silica gel column (eluent 1:5 ethyl acetate/dichloromethane) to give the title compound as a pale red solid (0.183 g, 46%). Melting point: 93−95 °C. Selected IR (KBr, cm^{-1}): 1607(s), 1580(m), 1503(s), 1459(m), 1435(m), 1324(m), 1290(s), 1266(m), 1208(s), 1157(m), 1094(m), 1032(s), 825(s), 745(m), 688(m), 493(m). ^{1}H NMR (CD_2Cl_2, δ), 8.20−6.18 (m, 16H), 3.83−3.40 (m, 14H) ppm. ^{13}C NMR (CD_2Cl_2, δ), 160.5, 158.3, 133.4, 132.5, 131.2, 128.7, 127.7, 104.0, 98.2, 97.9, 55.4, 55.3, 28.2 ppm. ^{31}P NMR (CD_2Cl_2, δ), 46.4 (s, J(P,Se) = 373/759 Hz). ^{77}Se NMR (CD_2Cl_2, δ), 338.7 (d, J(P,Se) = 370 Hz), −213.0 (d, J(P,Se) = 756 Hz) ppm. Accurate mass measurement [CI$^+$, m/z]: found 836.8352 [M + H]$^+$, calculated mass for $C_{30}H_{30}O_4P_2Se_4H$: 836.8356.

Synthesis of Compounds 6 and 7. A suspension of *N*′-(benzo[*d*][1,3]dioxol-5-ylmethylene)benzohydrazide **5** (0.268 g, 1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in 20 mL of dry toluene was refluxed for 7 h. Upon cooling to room temperature and removing toluene, the residue was purified by silica gel column to give the compounds **6** (eluent dichloromethane) and **7** (eluent 1:5 ethyl acetate/dichloromethane).

3,6-Bis(benzo[*d*][1,3]dioxol-5-yl)-2,5-diphenyl-1,4,2,5-diselenadiphosphinane 2,5-diselenide (6). Yellow paste (0.11 g, 14%). Two diastereoisomers were found in ca. 1:1 intensity ratio in multi-NMR spectra. Selected IR (KBr, cm^{-1}): 1502(m), 1487(s), 1440(s), 1358(m), 1250(s)1184-(m), 1095(m), 1038(s), 926(s), 811(s), 746(m), 689(m), 506(m), 421(m). ^{1}H NMR ($CDCl_3$, δ), 8.20−8.15 (m, 1H), 7.96−7.88 (m, 1H), 7.85 (d, J(P,H) = 1.8 Hz, 2H), 7.44 (dd, J(H,H) = 8.1 Hz, J(P,H) = 1.8 Hz, 4H), 7.92−7.87 (m, 4H), 7.56−6.68 (m, 20H), 4.55 (s, 4H), 4.51 (s, 4H), 4.05 (d, J(P,H) = 11.0 Hz, 2H), 3.95 (d, J(P,H) = 14.2 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, δ), 148.1, 148.0, 147.7, 147.0, 140.1, 139.5, 133.3, 132.2, 131.9, 131.1, 130.6, 129.2, 129.0, 128.3, 126.9, 122.6, 121.7, 75.5, 55.1, 52.1 (d, J(P,C) = 28.6 Hz), 47.2 (d, J(P,C) = 36. Hz) ppm. ^{31}P NMR ($CDCl_3$, δ), 48.5 (s, J(P,Se) = 343/783 Hz), 46.6 (s, J(P,Se) = 363/767 Hz). ^{77}Se NMR ($CDCl_3$, δ), 491.7 (d, J(P,Se) = 343 Hz), 348.0 (d, J(P,Se) = 363 Hz), −219.8 (d, J(P,Se) = 767 Hz), −257.1 (d, J(P,Se) = 783 Hz) ppm. Accurate mass measurement [CI$^+$, m/z]: found 804.7725 [M + H]$^+$, calculated mass for $C_{28}H_{22}O_4P_2Se_4H$: 804.7721.

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2-(Benzo[*d*][1,3]dioxol-5-yl)-5-(*p*-tolyl)-1,3,4-selenadiazole (7). Grey solid (0.190 g, 55%). Melting point: 93−95 °C. Selected IR (KBr, cm^{-1}): 1607(m), 1504(m), 1461(vs), 1265(vs), 1181(m), 1112(m), 1066(m), 1036(s), 935(m), 864(s), 823(s), 596(m). ^{1}H NMR ($CDCl_3$, δ), 7.85 (d, J(H,H) = 8.2 Hz, 2H), 7.54−7.43 (m, 3H), 7.32 (d, J(H,H) = 8.2 Hz, 2H), 6.92 (d, J(H,H) = 8.0 Hz, 1H), 6.10 (s, 2H), 2.44 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, δ), 150.1, 148.5, 141.7, 130.5, 129.8, 128.5, 127.4, 124.2, 108.7, 107.7, 102.1, 21.2 ppm. ^{77}Se NMR ($CDCl_3$, δ), 679.0 ppm. Accurate mass measurement [CI^+, m/z]: found 345.0138 $[M + H]^+$, calculated mass for $C_{16}H_{12}N_2O_2SeH$: 345.0142.

General Procedure for the Synthesis of Compounds 9a−d. A suspension of benzohydrazide **8a−d** (1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in 20 mL of dry toluene was refluxed for 7 h. Upon cooling to room temperature and removing toluene in vacuum, the residue was purified by silica gel column (eluent 1:1 hexane/dichloromethane) to give compounds **9a−d**.

7a-Methyl-5,6-diphenyl-2-(*p*-tolyl)-6,7,7a-trihydro-[1,2]azaphospholo[5,1-*b*][1,3,4]selenadiazole 5-selenide (9a). Light-gray solid (0.240 g, 52%). Melting point: 78−80 °C. Selected IR (KBr, cm^{-1}): 1605(m), 1542(m), 1494(m), 1435(s), 1375(m), 1281(s), 1181(s), 1136(s), 1100(s), 922(s), 817(s), 763(s), 746(s), 690(s), 588(vs), 513(m), 399(m). ^{1}H NMR ($CDCl_3$, δ), 8.12−8.06 (m, 2H), 7.63−7.54 (m, 5H), 7.34−7.32 (m, 3H), 7.17 (d, J(H,H) = 7.7 Hz, 2H), 7.14 (m, 2H), 5.32 (s, 0.5H from CH_2Cl_2), 4.27−4.20 (m, 1H), 3.83−3.74 (m, 1H), 2.88−2.75 (m, 1H), 2.38 (s, 3H), 2.13 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, δ), 159.4 (d, J(P,C) = 7.8 Hz), 141.1, 132.6, 132.5 (d, J(P,C) = 3.4 Hz), 132.2 (d, J(P,C) = 11.9 Hz), 132.1 (d, J(P,C) = 86.6 Hz), 130.4, 129.4, 129.3, 128.7 (d, J(P,C) = 13.5 Hz), 128.5, 128.4, 128.1 (d, J(P,C) = 3.1 Hz), 82.3 (d, J(P,C) = 8.0 Hz), 49.6 (d, J(P,C) = 54.4 Hz), 42.4 (d, J(P,C) = 6.4 Hz), 35.1 (d, J(P,C) = 5.0 Hz), 21.5 ppm. ^{31}P NMR ($CDCl_3$, δ), 65.2 (s, J(P,Se) = 818 Hz) ppm. ^{77}Se NMR ($CDCl_3$, δ), 625.4 (s) ppm, −285.5 (d, J(P,Se) = 818 Hz) ppm. Accurate mass measurement [CI^+, m/z]: found 531.0001 $[M + H]^+$, calculated mass for $C_{24}H_{23}N_2PSe_2H$: 531.0004.

6-(2-Methoxyphenyl)-5-phenyl-2-(*p*-tolyl)-6,7,7a-trihydro-[1,2]azaphospholo[5,1-*b*][1,3,4]selenadiazole 5-selenide (9b). Gray solid (0.240 g, 50%). Melting point: 53−55 °C. Selected IR (KBr, cm^{-1}): 1600(m), 1492(s), 1460(s), 1435(s), 1281(m), 1246(vs), 1179(m), 1104(s), 1027(m), 924(m), 816(m), 747(vs), 689(m), 569(m). ^{1}H NMR ($CDCl_3$, δ), 8.22−8.05 (m, 1H), 7.68−7.50 (m, 5H), 7.42−7.38 (m, 1H), 7.24−7.15 (m, 3H), 7.07−7.00 (m, 1H), 6.75−6.61 (m, 1H), 6.47−6.37 (m, 1H), 4.79−4.70 (m, 1H), 3.94−3.75 (m, 1H), 3.50−3.40 (m, 1H), 3.12 (s, 3H), 2.46−2.39 (m, 1H), 2.37 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, δ), 156.9 (d, J(P,C) = 5.1 Hz, Azole-C), 155.8 (d, J(P,C) = 9.5 Hz), 140.7, 132.2 (d, J(P,C) = 12.3 Hz), 131.9 (d, J(P,C) = 3.3 Hz), 130.1, 129.4, 128.6, 128.1 (d, J(P,C) = 13.7 Hz), 127.6, 126.3, 122.1, 120.5 (d, J(P,C) = 3.1 Hz), 109.7 (d, J(P,C) = 3.1 Hz), 70.4 (d, J(P,C) = 8.0 Hz), 54.4, 44.7 (d, J(P,C) = 54.4 Hz), 36.4 (d, J(P,C) = 7.8 Hz), 21.5 ppm. ^{31}P NMR ($CDCl_3$, δ), 78.6 (s, J(P,Se) = 816 Hz). ^{77}Se NMR ($CDCl_3$, δ), 496.1 (s) ppm, −286.8 (d, J(P,Se) = 816 Hz) ppm. Accurate mass measurement [CI^+, m/z]: found 546.9954 $[M + H]^+$, calculated mass for $C_{24}H_{23}ON_2PSe_2H$: 546.9953.

5,6-Biphenyl-2-(*p*-tolyl)-6,7,7a-trihydro-[1,2]-azaphospholo[5,1-*b*][1,3,4]selenadiazole 5-selenide (9c). Gray solid (0.275 g, 61%). Melting point: 82−83 °C. Selected IR (KBr, cm^{-1}): 1605(m), 1573(m), 1493(m), 1434(s), 1307(m), 1279(s), 1180(s), 1087(s), 922(s), 815(s), 763(s), 745(s), 691(vs), 645(m), 609(m), 563(s), 521(s). ^{1}H NMR ($CDCl_3$, δ), 8.04−7.98 (m, 2H), 7.63−7.52 (m, 5H), 7.35−7.32 (m, 3H), 7.19−7.12 (m, 4H), 6.43−6.37 (m, 1H), 4.21−4.13 (m, 1H), 3.94−3.39 (m, 1H), 3.06−2.92 (m, 1H), 2.38 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, δ), 156.9 (d, J(P,C) = 9.6 Hz), 133.1, 132.5 (d, J(P,C) = 3.3 Hz), 132.1 (d, J(P,C) = 12.1 Hz), 130.1, 129.2, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1 (d, J(P,C) = 3.7 Hz), 70.3 (d, J(P,C) = 8.1 Hz), 51.8 (d, J(P,C) = 53.8 Hz), 37.1 (d, J(P,C) = 7.7 Hz), 21.5 ppm. ^{31}P NMR (CD_2Cl_2, δ), 77.4 (s, J(P,Se) = 822 Hz). ^{77}Se NMR (CD_2Cl_2, δ), 521.5 (s) ppm, −273.2 (d, J(P,Se) = 822 Hz) ppm. Accurate mass measurement [CI^+, m/z]: found 516.9844 $[M + H]^+$, calculated mass for $C_{23}H_{21}N_2PSe_2H$: 516.9846.

7a-Methyl-2,5,6-triphenyl-6,7,7a-trihydro-[1,2]-azaphospholo[5,1-*b*][1,3,4]selenadiazole 5-selenide (9d). Gray solid (0.310 g, 60%). Melting point: 75−77 °C. Selected IR (KBr, cm^{-1}): 1545(m), 1493(m), 1436(s), 1274(s), 1175(m), 1099(s), 1026(m), 923(s), 766(s), 747(m), 692(vs), 624(s), 566(m), 520(m), 505(s). ^{1}H NMR ($CDCl_3$, δ), 8.12−8.06 (m, 2H), 7.74−7.71 (m, 2H), 7.66−7.55 (m, 3H), 7.45−7.28 (m, 6H), 7.15−7.11 (m, 2H), 4.29−4.21 (m, 1H), 3.84−3.75 (m, 1H), 2.89−2.76 (m, 1H), 2.14 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, δ), 159.2 (d, J(P,C) = 8.0 Hz), 133.1, 132.8, 132.5 (d, J(P,C) = 3.6 Hz), 132.2 (d, J(P,C) = 12.0 Hz), 130.7, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1 (d, J(P,C) = 3.7 Hz), 82.5 (d, J(P,C) = 8.1 Hz), 49.6 (d, J(P,C) = 54.4 Hz), 42.4 (d, J(P,C) = 6.4 Hz), 35.1 (d, J(P,C) = 4.8 Hz) ppm. ^{31}P NMR ($CDCl_3$, δ), 78.8 (s, J(P,Se) = 820 Hz). ^{77}Se NMR ($CDCl_3$, δ), 625.8 (s) ppm, −284.2 (d, J(P,Se) = 820 Hz) ppm. Accurate mass measurement [CI^+, m/z]: found 516.9849 $[M + H]^+$, calculated mass for $C_{23}H_{21}ON_2PSe_2H$: 516.9851.

Synthesis of 4-Methyl-3-(2-(4-methylbenzylidene)-hydrazinyl)-2,5-diphenyl-1,2-selenaphospholane 2-selenide (11). A suspension of 4-methyl-*N*′-(2-methyl-3-phenylallylidene)benzohydrazide **10** (0.278 g, 1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in 20 mL of dry toluene was refluxed for 7 h. Upon cooling to room temperature and removing toluene in vacuum, the residue was purified by silica gel column (eluent 1:1 hexane/dichloromethane) to give the titled compound as white solid (0.255 g, 55%). Melting point: 70−72 °C. Selected IR (KBr, cm^{-1}): 1608(m), 1493(m), 1452(m), 1435(s), 1375(m), 1307(m), 1283(m), 1180(m), 1091(vs), 942(s), 814(s), 746(s), 696(vs), 558(m), 511(m), 475(m). ^{1}H NMR ($CDCl_3$, δ), 8.11−8.04 (m, 2H), 7.83 (d, J(P,H) = 3.1 Hz, 2H), 7.53−7.31 (m, 7H), 7.07−7.00 (m, 4H), 4.18−4.15 (m, 1H), 2.80−2.71 (m, 2H), 2.35 (m, 3H), 1.17 (d, J(P,H) = 6.5 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, δ), 144.8, 138.1 (d, J(P,C) = 3.3 Hz), 132.7 (d, J(P,C) = 12.4 Hz), 132.6, 131.7, 131.5 (d, J(P,C) = 3.6 Hz), 132.1, 129.0, 128.7, 128.5, 128.4, 126.4, 112.0, 53.5, 43.8 (d, J(P,C) = 14.0 Hz), 29.7, 21.4, 16.6 (d, J(P,C) = 12.7 Hz) ppm. ^{31}P NMR ($CDCl_3$, δ), 59.9 (s, J(P,Se) = 382/748 Hz). ^{77}Se NMR ($CDCl_3$, δ), 387.1 (d, J(P,Se) = 382 Hz), −207.8 (d, J(P,Se) = 749 Hz) ppm. Accurate mass measurement [CI^+, m/z]: found 533.0002 $[M + H]^+$, calculated mass for $C_{24}H_{25}N_2PSe_2H$: 533.0004.

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■ ASSOCIATED CONTENT

Supporting Information

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CIF are available from the Cambridge Crystallographic Data Centre (CIF, PDF)

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Notes

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